

## **Electrodes for Polymer Electrolyte Membrane Operation on Hydrogen/Air and Reformate/Air**

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### **Objectives**

- Improve tolerance to carbon monoxide (CO) and study the effect of other fuel and air impurities.
- Improve the efficiency of the fuel cell electrodes while lowering the dependence on Pt loadings.
- Improve overall polymer electrolyte membrane (PEM) fuel cell operating efficiency.

### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance

### **Approach**

- Investigate the use of reconfigured anodes to improve fuel cell performance in the presence of trace levels of CO impurities.
- Evaluate new anode catalysts for CO tolerance.
- Investigate porosity and fuel cell performance as functions of the ionomer content in the catalyst layer.
- Evaluate new cathode catalyst materials for higher operating efficiencies at lower precious metal loadings.
- Investigate the effect of potential ambient air impurities on cathode performance.

### **Accomplishments**

- Demonstrated increased tolerance to 500 ppm CO/reformate using the reconfigured anode.
- Demonstrated 1000 hrs of operation of the 1 wt% Pt-10 wt% Ru anode catalyst running on H<sub>2</sub>/air with 50 ppm CO and 4% air bleed.
- Demonstrated the performance degradation of a Pt-Cr cathode catalyst after 500 hours of operation.
- Demonstrated how the catalyst layer porosity and fuel cell performance correlate with catalyst layer Nafion content.
- Established the negative effects of SO<sub>2</sub> and NO<sub>2</sub> on cathode performance.

## Future Directions

- Investigate alternative catalyst materials for use in reconfigured anodes.
  - Continue the evaluation of new potential CO tolerant catalysts.
  - Screen new potential cathode catalyst materials, particularly with low Pt content.
  - Continue to develop improved membrane electrode assembly (MEA) fabrication protocols.
  - Investigate methods to mitigate the effects of SO<sub>2</sub> and NO<sub>2</sub> on fuel cell performance.
  - Investigate the effect of other potential ambient air impurities on fuel cell performance.
  - Investigate strategies for recovering the performance of fuel cells whose catalysts have been poisoned by H<sub>2</sub>S and SO<sub>2</sub>.
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## Introduction

The reforming of hydrocarbon fuels is one of the leading processes under consideration for producing hydrogen to power PEM fuel cells. However, the hydrogen stream generated by the reforming process can contain volatile chemical compounds that significantly diminish fuel cell performance. Two approaches to solving this problem are to improve the efficiency of the reformation process to lower the levels of harmful impurities, or to modify the fuel cell itself to be more tolerant toward those compounds. This study has taken the latter approach, where ways were investigated to improve the anode performance in the presence of anticipated reformat impurities.

Fuel cell operation depends not only on hydrogen oxidation at the anode but also on oxygen reduction at the cathode. The oxygen reduction reaction plays a very significant role in limiting the operating efficiency of the fuel cell and is very dependent on high precious metal loadings in the catalyst layer. Improving the efficiency of the oxygen reduction reaction while lowering the precious metal loading is critical to commercialization of fuel cell technology for transportation applications. Also, recent awareness that impurities in the air stream can affect fuel cell performance has led to a more detailed investigation of some potentially harmful compounds commonly found in air.

## Approach

The impurity in the reformat stream expected to have the largest adverse affect on fuel cell

performance is carbon monoxide (CO). This gas is more strongly adsorbed on the surface of the catalyst than hydrogen, effectively blocking the sites where hydrogen oxidation would normally occur. One method to prevent this from happening is to remove the CO by oxidizing it to carbon dioxide, which does not adsorb on the catalyst, before it can reach and react with the anode surface. This can be accomplished by using the reconfigured anode developed by Los Alamos National Laboratory (LANL). The reconfigured anode has an outer, non-precious metal catalyst layer added to the standard MEA. Bleeding a low level of oxygen into the fuel stream results in preferential oxidation of CO at this outer layer. A second approach to solving the CO problem is to use an anode catalyst that is intrinsically more CO tolerant. For example, platinum/ruthenium alloys have been shown to be more CO tolerant than platinum alone and have the added advantage of containing a lower percentage of the expensive platinum metal component. Many new potential catalysts are submitted to LANL on a regular basis from both commercial and non-commercial sources. These materials are fabricated into MEAs using an established protocol, and then tested in fuel cells under standard operating conditions.

A third approach to identifying improved fuel cell anodes is to develop a better understanding of the kinetics and mechanisms associated with reactions of suspected impurities in the reformat stream with various catalyst materials. This information can potentially lead to alternative mitigation schemes. The mechanism for CO poisoning of platinum-based anode catalysts is fairly well understood; for other potential poisons and catalyst combinations, that may

not necessarily be the case. During this past review period, we have focused on catalyst interactions with hydrogen sulfide and ammonia, two very likely by-products in reformed fuels initially containing sulfur and nitrogen compounds.

A similar list of activities was undertaken to improve fuel cell cathode performance and can be summarized in the following outline:

- Develop new MEA fabrication methods to improve catalyst utilization.
- Work with catalyst suppliers to develop/test new catalyst formulations.
- Study the effect of catalyst layer structure on performance.
- Study the effects of suspected impurities present in air (sulfur dioxide, nitrogen oxides, particulates) on cathode performance.

## Results

Anode catalysts consisting of Pt-Ru alloys have been shown to be more tolerant to CO in the fuel stream than platinum alone. However, the commercially available materials are still expensive due to their high Pt contents. R. Adzic and co-workers from Brookhaven National Laboratory submitted a new catalyst for evaluation, with much lower platinum loading. This material contained only 1% platinum and 10% ruthenium, on a carbon support. A 1000-hour performance test was carried out using this catalyst in a fuel cell anode with a loading of  $17 \mu\text{g Pt}/\text{cm}^2$ , approximately 1/10 that of a normal loading. The results are shown in Figure 1. The voltage losses after 1000 hours of operation at fixed current were only 40 mV when the cell was operated on clean  $\text{H}_2$ , and 60 mV when operated with  $\text{H}_2$  containing 50 ppm CO and 4% air. This is an extremely promising result that could have a major impact on lowering fuel cell costs and bringing the technology closer to commercialization.

On the cathode side, the effects of two common air impurities were investigated: sulfur dioxide ( $\text{SO}_2$ ) and nitrogen dioxide ( $\text{NO}_2$ ). Figure 2 shows the performances of fuel cells whose cathodes are exposed to 1 ppm and 5 ppm of  $\text{SO}_2$ , respectively. Both levels of impurity degraded the fuel cell performance, and, as expected, the effect with the higher concentration was faster and more acute. In

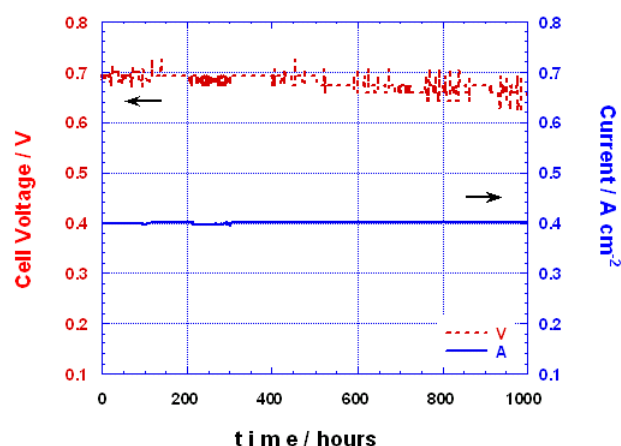


Figure 1. Low Pt Content Anode Durability Test at Constant Current

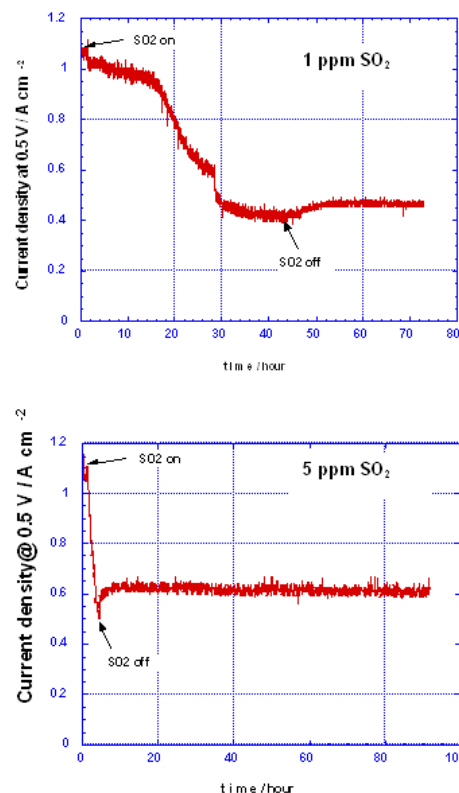


Figure 2. Effect of Sulfur Dioxide on Fuel Cell Performance

both cases, the cathode performance degradations were irreversible; the fuel cell did not recover after the  $\text{SO}_2$  was shut off and it was allowed to operate on clean air for many hours. Further characterization by

cyclic voltammetric measurements showed the  $\text{SO}_2$  (or a related species) was strongly adsorbed on the Pt catalyst surface.

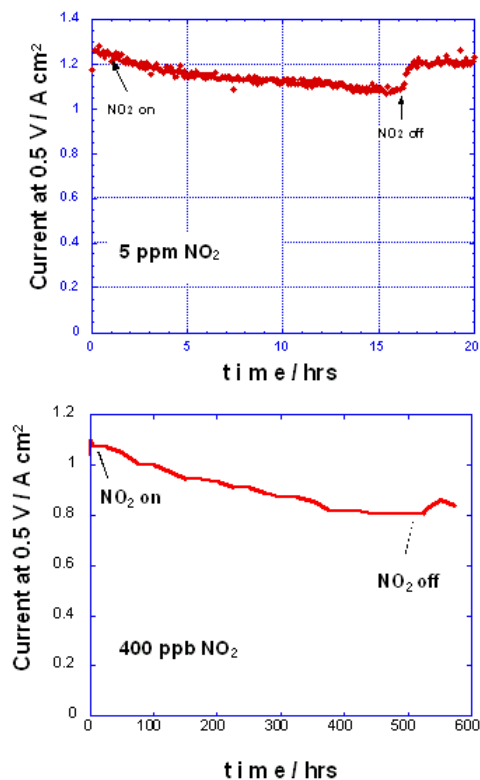
Nitrogen oxide has a similar negative effect on cathode performance, as shown in Figure 3. Performance degradation was less severe than with sulfur dioxide, but still significant. The degradation upon exposure to 5 ppm of  $\text{NO}_2$  for about 15 hours was reversible as the cell recovered its original performance when operated again with clean air. Long-term exposure to 0.4 ppm  $\text{NO}_2$  produced a slower negative effect on fuel cell performance that did not recover on operation with clean air. This data is still preliminary, and there is still no conclusive evidence to suggest the mechanism by which this impurity degrades performance. However, it is clear that the quality of the air stream entering the fuel cell is as important as the quality of the fuel stream and

must be of reasonably high purity to guarantee performance optimization and durability.

Further characterization of the catalyst layers of the MEA was also conducted with an aim toward optimizing fuel cell performance. For example, a measure of the porosity of the catalyst layer formed from recast Nafion showed that maximum porosity corresponded with optimum performance at a Nafion content of approximately 30%. It was also discovered that varying the fabrication materials and method could alter the surface morphology of the catalyst layer. Under certain conditions, a thin ionomer film formed on the outer surface of the catalyst layer. This film inhibited transport of reactant gases to the active catalyst sites and the removal of water formed at the cathode. The decrease in mass transport resulted in a drop in performance at high current densities.

## Conclusions

- We have shown that a level of 50 ppm CO in the fuel stream could be tolerated with a Pt/Ru catalyst at relatively low loading ( $17 \mu\text{g Pt}/\text{cm}^2$ ) when combined with air bleed. This catalyst was also shown to be quite stable under normal operating conditions, exhibiting a minimal drop in performance over 1000 hours.
- Some common air impurities,  $\text{SO}_2$  and  $\text{NO}_2$ , were also found to have a deleterious effect on fuel cell performance when admitted to the cathode air stream. These compounds will have to be removed prior to use in a fuel cell system to ensure continued performance and durability.
- The preparation method and materials affect the morphology of the catalyst layer in an MEA. The optimal performance observed at a Nafion loading of approximately 30% in the MEA correlates with a maximum in catalyst layer porosity. Under certain preparation conditions, a thin skin that inhibits molecular transport forms on the outer catalyst layer. This skin affects the fuel cell performance in the high current region of the operating curve.



**Figure 3.** Effect of Nitrogen Dioxide on Fuel Cell Performance

**FY 2003 Presentations**

1. K. Sasaki, Y. Mo, J. X. Wang, F. A. Uribe and R. R. Adzic. "Pt Submonolayer Electrocatalysts for H<sub>2</sub> Oxidation and O<sub>2</sub> Reduction". 203<sup>rd</sup> Meeting of The Electrochemical Society Meeting, Paris, France. April 2003. Abstr. 2679.
2. K. Sasaki, Y. Mo, J. X. Wang, M. Balasubramanian, F. A. Uribe, J. McBreen, R. R. Adzic. "Pt Submonolayers on Metal Nanoparticles - Novel Electrocatalysts for H<sub>2</sub> Oxidation and O<sub>2</sub> Reduction". Accepted in *Electrochimica Acta* (2003).
3. J. Xie, F. H. Garzon, T. Zawodzinski and W. Smith. "The Ionomer Segregation in Composite Membrane Electrode Assemblies and the Effect on the Performance of PEM Fuel Cells". 203<sup>rd</sup> Meeting of The Electrochemical Society Meeting, Paris, France. April 2003. Abstr. 1185.
4. P. A. Adcock, E. L. Brosha, F. H. Garzon, and F. A. Uribe. "Characterization of Potential Catalysts for Carbon Monoxide Removal from Reformate Fuel for PEM Fuel Cells". *Mat. Res. Soc. Symp. Proc.* Vol. 756 (2003) 365.
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6. G. Bender, M. S. Wilson and T. A. Zawodzinski. "Further Refinements in the Segmented Cell Approach to Diagnosing Performance in Polymer Electrolyte Fuel Cells", in print at *Journal of Power Sources*.
7. F. Uribe. "Coping with Fuel Impurities in PEM Fuel Cells". Advances in Materials for Proton Exchange Membrane Fuel Cell Systems. Division of Polymer Chemistry, ACS. Asilomar, CA, February 2003.
8. W. Smith. "Fuel Cell Research and Development at Los Alamos National Lab". Fuel Cell Seminar. Palm Springs, CA, November 2002.
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11. G. Bender and T. A. Zawodzinski. "Spatial Distribution of the CO Transient Response of a PEFC". Third International Symposium On Proton Conducting Membrane Fuel Cells, 202nd Meeting of The Electrochemical Society Meeting, Salt Lake City, Utah. October 2002.
12. F. Uribe and T. A. Zawodzinski. "A Study of Polymer Electrolyte Fuel Cell Performance at High Voltages. Dependence on Cathode Catalyst Layer Composition and on Voltage Conditioning". *Electrochimica Acta*, 47(2002) 3799.